916. *Low-temperature Magnetic Properties of Some Uranium Oxides.*

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The magnetic susceptibilities of UO_2, $UO_{2\cdot 1}$, U_4O_9, U_3O_7, and U_3O_8 at temperatures between 1·5° and 44°K have been determined using an a.c. inductance method. The susceptibility of U_3O_8 rises to a sharp maximum at 4·2°K, with smaller effects at 8° and at 25·3°K. The susceptibility of UO_2 reaches a maximum at 29°K and remains constant between 25° and 2°K. A maximum in the susceptibility–temperature plot for U_4O_9 at 6·4°K occurs also in the plots for $UO_{2\cdot 1}$ and U_3O_7 and appears to be primarily due to the inclusion of interstitial oxygen ions in the UO_2 lattice, independent of the precise nature of subsequent ordering effects.

Chemical investigation of the uranium–oxygen system has shown the existence of a number of oxide phases with ideal compositions UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3.[1] The phases which are stable at high temperatures (>600°) are (i) UO_2, with the simple fluorite structure, (ii) UO_{2+x}, a non-stoicheiometric phase related to UO_2 by the incorporation of additional oxygen atoms in randomly-distributed interstitial positions in the fluorite lattice, (iii) U_4O_9, with a small range of homogeneity, where U_4O_{9-y} is again related to UO_{2+x} but with the interstitial oxygen atoms now in an ordered array, giving a complicated structure with 832 atoms in the unit cell;[2] (iv) U_3O_{8-z}, with an orthorhombic structure related to that of U_3O_8,[3] and (v) U_3O_8 itself, which may undergo a structural transition when heated.[4] The oxidation of UO_2 can commence at low temperature, even at room temperature, and a number of phases of composition close to U_3O_7 have been identified.[5-7] These are tetragonal distortions of the fluorite structure of UO_2 and are again related to UO_{2+x} and U_4O_9, having been formed by the incorporation of interstitial oxygen in the fluorite lattice of UO_2. These tetragonal oxides are unstable at high temperature, disproportionating to U_4O_9 and U_3O_{8-z}. The relationship between all these structures has been reviewed.[1]

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[1] Roberts, *Quart. Rev.*, 1961, **15**, 442.
[2] Belbeoch, Piekarski, and Perio, *Acta Cryst.*, 1961, **14**, 837.
[3] Hoekstra, Siegel, Fuchs, and Katz, *J. Phys. Chem.*, 1955, **59**, 136.
[4] Siegel, *Acta Cryst.*, 1955, **8**, 617.
[5] Anderson, Roberts, and Harper, *J.*, 1955, 3946.
[6] Hoekstra, Santoro, and Siegel, *J. Inorg. Nuclear Chem.*, 1961, **18**, 166.
[7] Belbeoch, Piekarski, and Perio, *J. Nuclear Materials*, 1961, **3**, 60.

The magnetic behaviour of this system attracted interest for two reasons. First, the magnetic susceptibility was thought to be a good means of studying the phase changes occurring at various fixed oxygen : uranium ratios, and, secondly, the prospect of being able to dilute the uranium ion progressively in a continuous series of oxides of gradually increasing oxygen content seemed very likely to produce information on interactions betweeen uranium ions. A number of workers have already carried out experiments along these lines [8-10] and the results have led to a number of general conclusions regarding the electronic configuration of the uranium ion and the change in valency state as a function of the oxygen : uranium ratio. Arrott and Goldman [10] made susceptibility measurements on oxides of a number of intermediate compositions between UO_2 and U_3O_8, but unfortunately the interpretation of their results is complicated by a lack of knowledge of the phases actually present in their samples. It now seems certain that the phase boundaries deduced from their results are incorrect, perhaps owing to the compositions of their samples not being known with sufficient accuracy.

The present work is also concerned with susceptibility measurements on a number of oxides, but in this case advantage has been taken of the many recent studies of the uranium–oxygen system to prepare specimens which are thoroughly characterised both chemically and structurally. In each case the phases present have been deduced both from the thermal history and composition of the sample, and also from X-ray diffraction measurements. The measurements of susceptibility were confined to low temperatures (below 44°K), where anomalous behaviour may be expected to occur, and in particular the range below 10°K has been studied in greater detail than in earlier researches.

The work has been carried out primarily in order to establish the experimental values on a sound basis. Detailed interpretation is not attempted, as a complete explanation of the magnetic properties is not possible from susceptibility data alone. This is particularly true here because of the complex structure of many of the oxides and the fact that only one of them, UO_2, has a diamagnetic isomorph, ThO_2.

EXPERIMENTAL

Susceptibility Measurement.—The apparatus used for susceptibility measurement was similar to an earlier design by McKim and Wolf,[11] so that only the principles will be described here. An a.c. Hartshorn bridge operating at 175 cycles/sec. is used to measure the mutual inductance of a specially wound coil, before and after moving the paramagnetic specimen a fixed distance along the coil axis. The observed change in mutual inductance is then proportional to the susceptibility, χ, of the specimen. The apparatus is calibrated by making measurements on a known weight of manganous ammonium sulphate hexahydrate. The susceptibility measurement is therefore carried out in the oscillatory magnetic field produced by the primary winding of the coil, and from practical considerations it was found convenient to operate with this field set at approximately 40 oersted.

This relatively small value of measuring field and its oscillatory character made the method very sensitive to out-of-phase effects associated with ferromagnetic and electrically conducting materials. For this reason the method could only be used for measurements on dielectric material, but by the same token the detection of ferromagnetic impurities was comparatively simple. In addition to large out-of-phase effects, ferromagnetic impurities tended to exhibit a susceptibility dependent on the magnitude of the measuring field, and one of the routine checks at the start of each experiment therefore consisted in measuring χ at a number of different primary fields between 2 and 100 oersted. All specimens which exhibited either out-of-phase or field-dependent effects were necessarily discarded from the investigation, since with the small range of magnetic field available from the coil windings, the ferromagnetic behaviour could not be quantitatively distinguished from paramagnetic behaviour as can be done, for instance, on a Faraday balance.

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[8] Dawson and Lister, *J.*, 1950, 2181; 1952, 5041.

[9] Trzebiatowski and Selwood, *J. Amer. Chem. Soc.*, 1950, **72**, 4504.

[10] Arrott and Goldman, *Phys. Rev.*, 1957, **108**, 948.

[11] McKim and Wolf, *J. Sci. Instr.*, 1957, **34**, 64.

Specimen containers were made from " Teflon," which can be cleaned very thoroughly by immersion in boiling aqua regia. The susceptibility of the container, which was measured in a separate experiment, was applied as a correction to the total magnetic susceptibility, but even for the magnetically weakest specimens this never amounted to more than 3%. The sensitivity of the apparatus was such that the smallest susceptibilities could be measured with a relative accuracy of 0·3% at 4·2°K (500 mg. samples), and an absolute accuracy in any one measurement estimated to be better than ±1%.

Measurements in most cases were made throughout the temperature range 1·6—44°K. For the liquid helium and hydrogen temperature ranges, 1·6—4·2°K and 14—20·4°K, respectively, the vapour pressure of the liquid was used to measure the temperature. For the range 4·2—14°K a novel method, based on the known susceptibility variation of manganous ammonium sulphate, was used. Details of this have been described elsewhere.[12] Temperatures above 20·4°K were measured by using the mutual inductance coil winding as a copper resistance thermometer, a method which has also been described in more detail elsewhere.[13]

Preparation of Specimens.—The starting material for most of the preparations was a specimen of " spectroscopically pure " U_3O_8 obtained from Johnson Matthey, and designated S.0. Typical analyses of this material show the absence of detectable quantities of Ag, Al, As, Au, B, Ba, Be, Br, Ca, Cd, Co, Cr, Cs, Fe, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, and Zr, with Cu <1 p.p.m. The susceptibility of a sample of this material was the lowest measured for U_3O_8, lower than that of a second sample from Johnson Matthey (S.0./A), and lower than values for U_3O_8 samples prepared from commercially available oxides from American and British sources, S.5 and S.6 (see below). On the principle that for such a magnetically weak substance, any impurities would tend to *raise* the susceptibility, S.0 was considered to be purer than any of the other samples.

S.1. $UO_{2\cdot00}$ was prepared by reducing S.0 U_3O_8 with carbon monoxide at 800° and pumping at 850°. It was sealed *in vacuo* and transferred to the Teflon specimen-container in a box filled with carbon dioxide gas from subliming " Drikold." After the susceptibility measurement the sample was analysed (by back-reduction with carbon monoxide to $UO_{2\cdot00}$) as $UO_{2\cdot012}$; hence, during measurement, the sample would be close to $UO_{2\cdot00}$, and certainly contain much less oxygen than $UO_{2\cdot01}$.

S.2. $UO_{2\cdot03}$ was made by reducing S.0 U_3O_8 with hydrogen at 800° and cooling in hydrogen. The sample was exposed to air at room temperature resulting in a final composition of approximately $UO_{2\cdot03}$. This material was used as a starting point for the preparation of samples of U_4O_9 by two different methods.

S.3. U_4O_9 was made from S.2 UO_2 by reduction to $UO_{2\cdot00}$ with carbon monoxide at 600° and controlled oxidation with a measured quantity of oxygen to $UO_{2\cdot23}$ at 150°. The sample was annealed *in vacuo* at 250° for 2 hr. *X*-Ray examination showed a cubic phase, $a_0 =$ 5·441 Å, not very well crystalline, with a trace of $UO_{2\cdot00}$ remaining. The sample then consisted mainly of a cubic phase resembling U_4O_{9-y}, but, in view of the low temperature of annealing and the poor crystallinity, some concentration gradient of oxygen may have remained in the oxide particles.

S.4. U_4O_9 was prepared by heating stoicheiometric quantities of S.2 UO_2 and S.0 U_3O_8 in a vacuum for 5 days at 850° and cooling the product for 2 days to room temperature. *X*-Ray examination showed only one cubic phase ($a = 5\cdot444$ Å) with some weak lines attributable to a few percent of residual U_3O_8. The sample therefore consisted of U_4O_9 with a trace of U_3O_8. At the end of the series of experiments, the composition of this sample was determined as $UO_{2\cdot31}$, by ignition to U_3O_8; this is as expected from the *X*-ray results.

S.1/1. $UO_{2\cdot1}$ was made by oxidising S.1 UO_2 in a limited, measured quantity of oxygen to $UO_{2\cdot098}$ at 180°, with subsequent annealing at 180° for 24 hr. *X*-Ray examination showed a single, cubic phase ($a = 5\cdot464$ Å). The configuration for this composition in thermodynamic equilibrium at 180° is a mixture of UO_2 and U_4O_9, but it is evident that the temperature was not high enough for this phase separation to have occurred. It seems probable that this sample is analogous to the homogeneous UO_{2+x} phases, containing interstitial oxygen in the fluorite lattice, which are truly stable at higher temperatures.[4]

S.1/2. $UO_{2\cdot1}$ was made by annealing S.1/1 $UO_{2\cdot1}$ for 2 hr. in a vacuum at 850°, at which

[12] Leask and Wolf, *Proc. Int. Cong. Refrigeration*, Copenhagen, 1957, **1**, 179.

[13] Leask, Orbach, Wolf, and Powell, to be published.

temperature it would be a homogeneous, cubic UO_{2+x} phase, and cooling rapidly. Slight oxidation occurred, and the composition is probably the same as that of S.1/3, which was analysed as $UO_{2\cdot122}$. *X*-Ray examinations showed $UO_{2\cdot00}$ lines and a much broadened set of lines in the U_4O_9 position. Division into the two phases had therefore occurred, but may not have been complete owing to the rather rapid cooling through the phase boundary.

S.1/3. $UO_{2\cdot1}$ was made by annealing S.1/2 $UO_{2\cdot1}$ in a sealed tube at 500° for 16 hr. and at 450° for 30 hr., with slow cooling. *X*-Ray examination showed two crystalline cubic phases. The sample consisted of a mixture of $UO_{2\cdot00}$ and U_4O_{9-y}; it was handled in an atmosphere of carbon dioxide, and, since subsequent analysis gave the accurate composition as $UO_{2\cdot122}$, S.1/2 cannot have been more highly oxidised than this.

S.1/3*a*. U_3O_7 was prepared by oxidising S.1/3 in air at 180° for 3 days, and annealing the product in an evacuated tube at 300° for 14 days. *X*-Ray examination showed a trace of U_3O_8 with the major phase tetragonal ($a = 5{\cdot}372$ Å, $c = 5{\cdot}545$ Å, $c/a = 1{\cdot}032$); this is the phase designated as β-U_3O_7 by Hoekstra, Santoro, and Siegel.[6] Two samples of S.1/3a were analysed as $UO_{2\cdot317}$ and $UO_{2\cdot308}$, giving a mean composition of $UO_{2\cdot31}$.

C.4. UO_2 was prepared by reducing in carbon monoxide at 850° a sample of composition $UO_{2\cdot045}$; this had been obtained by oxidation in air at room temperature of UO_2 originally prepared from " nuclear grade " ammonium diuranate.

S.5. (U_3O_8). UO_2, *ex* Mallinckrodt Chemical Works, was heated in air at 850° for 24 hr. to form U_3O_8.

S.6. (U_3O_8). A pure grade of ammonium diuranate was dissolved in acid and the uranium extracted into ether, and re-extracted into aqueous solution. The uranium was precipitated by adding ammonia, and ignited in air at about 850° to form U_3O_8.

Spectrographic analysis of samples S.5 U_3O_8 and X.6 U_3O_8 gave the following results, in p.p.m.:

	Fe	Ni	Mn	V	Cr	W	Si	Cu	Co	Ta	Mo
S. 5	15	<2	<5	<1	1	<200	—	2	<5	<200	<4
S. 6	20	14	<1	<5	<1	<200	400	25	<10	<200	<4

RESULTS AND DISCUSSION

U_3O_8.—As this compound was the starting material for all the other uranium oxides, it was unfortunate that its susceptibility was in fact less-well determined than any of the others. Four different U_3O_8 specimens (S.0, S.0/A, S.5, S.6) were examined at 4·2°K and it was found that for all of these the measured susceptibility was somewhat dependent on the magnitude of the measuring field with a corresponding out-of-phase component of susceptibility. Only in the case of specimen S.0 were these " ferromagnetic " effects negligibly small, since the absolute susceptibility of this sample was also some 30% lower than that of the other U_3O_8 specimens. S.0 was considered to be the purest U_3O_8 material and used as a starting point for the other preparations. It is probable that the small out-of-phase effects which were observed were not, in fact, due to a ferromagnetic impurity since they decreased to zero as the temperature was reduced from 4·2° to 1·5°K, and are therefore presumably connected with the susceptibility maximum found in this region.

The measurements were also complicated by the fact that the susceptibility of S.0 decreased with time, as can be seen from Fig. 1 which shows the results of two experiments eight months apart. On both occasions, the homogeneity of the stock material was checked by measuring three different samples at 4·2°K, and these agreed to within 0·7%. The time effect is not understood; phase changes do not occur in U_3O_8 at room temperature, and the material was kept in a closed (but not vacuum-tight) container. Nevertheless this effect does not mask the three maxima in the susceptibility, which occur at 4·2°, 8°, and 25·3°K. The 4·2°K peak was observed also with specimens S.5 and S.6, although, as already mentioned, the absolute value of the maximum was considerably greater. The peak at 25·3°K corresponds exactly with the small λ anomaly in the specific heat of U_3O_8 as observed by Westrum and Grönvold;[14] these workers, however, observed

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[14] Westrum and Grönvold, *J. Phys. and Chem. Solids*, 1962, **23**, 39.

no further anomalies down to 5°. Arrott and Goldman also reported no anomalous behaviour below 20°K for U_3O_8, although the present work agrees well with their result at 20°K.

$UO_{2\cdot0}$.—Fig. 2 shows the susceptibility as a function of temperature for two specimens of $UO_{2\cdot0}$. One specimen (C. 4) was measured in the range 2—20°K, the other (S.1) in the range 20—44°K, and it can be seen that the two sets of measurements join on well at 20°K. The results agree well with those by Dawson and Lister,[8] and with the general behaviour found by Arrott and Goldman,[10] except for the absolute value of the susceptibility below 24°K for which we find a value 6% higher. The peak in χ occurs at the same temperature as previously observed, and the temperature corresponding to $[\partial(\chi T)/\partial T]_{\text{max.}}$, ~29°K, agrees very well with the temperature corresponding to the λ anomaly in the UO_2 specific heat which occurs at 28·5°K.[15]

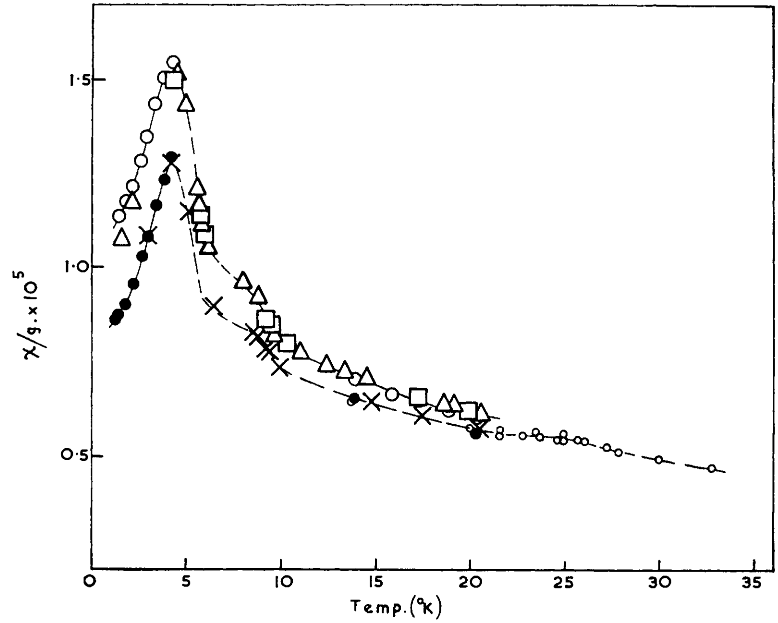

FIG. 1. Susceptibility of U_3O_8 (S.0) between 1·5° and 32°K. The different symbols refer to experimental points taken during a number of different experiments; they fall clearly into two main groups, which were taken eight months apart. These are shown by the two broken lines.

U_4O_9, $UO_{2\cdot1}$, and U_3O_7.—The results for all these compositions are shown in Fig. 3. The susceptibility maximum observed for U_4O_9 at 6·4°K was also indicated by the results of Arrott and Goldman, although they attributed it to the presence of impurities and/or foreign oxide phases. It seems certain from the present results that it is a property of U_4O_9. The results for the two samples S.3 and S.4 agreed closely, although the two samples had been prepared in very different ways and one of them contained a trace of UO_2 and the other a trace of U_3O_8. The magnetic behaviour is then not critically dependent on the details of preparation or on the detailed condition of the sample-particle size, crystallinity, composition, etc.

The origin of the maximum at 6·4°K is not clear, particularly since the specific-heat measurements on U_4O_9 showed no anomalous behaviour down to 5°K.[14] It is quite possible, however, that any effects at 6·4°K would have been missed in the specific-heat measurements, since rather few points were taken below 7°K.

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[15] Jones, Gordon, and Long, *J. Chem. Phys.*, 1952, **20**, 695.

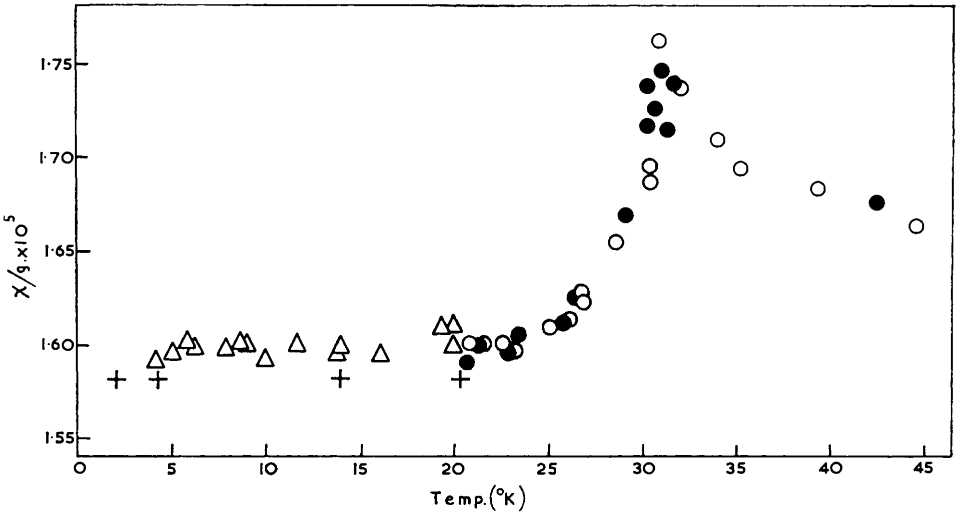

FIG. 2. Susceptibility of UO_2 between 2° and 44°K. The open and closed circles refer to measurements made on sample S.1 UO_2, the crosses and triangles to measurements made on sample C.4.

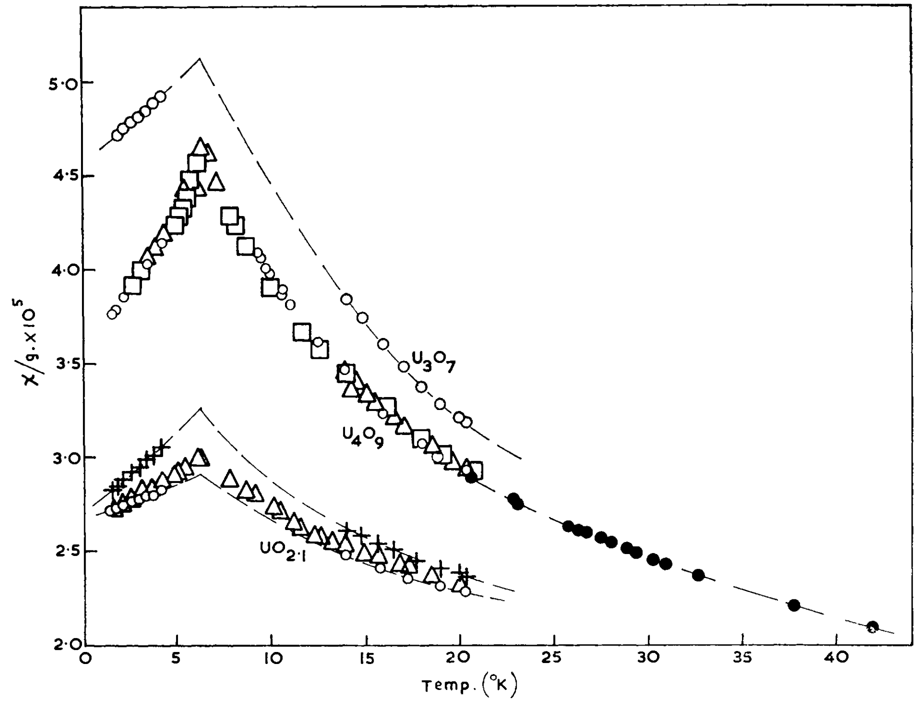

FIG. 3. Susceptibility per g. of U_4O_9, U_3O_7, and UO_2, as a function of temperature, showing the susceptibility maximum at 6·4°K. For U_4O_9 the different symbols refer to a number of experimental runs on each of the samples S.3 and S.4; for $UO_{2\cdot1}$, circles represent S.1/1, triangles S.1/2, and crosses S.1/3.

The major result of the examination of the $UO_{2\cdot1}$ and of the tetragonal $UO_{2\cdot3}$ samples was that the susceptibility maximum still occurred at 6·4°K (Fig. 3). The S.1/1—S.1/3 series varied from a rather poorly defined sample of composition $UO_{2\cdot098}$, probably cubic and analogous to the high-temperature UO_{2+x} phases, to a well-defined sample of $UO_{2\cdot122}$, which consisted of crystalline UO_2 and U_4O_9 phases, and yet the susceptibility was much the same throughout, tending to increase with increasing oxygen content. The true unit cell of U_4O_9 contains 832 atoms and is related to the UO_{2+x} structure, in which x oxygen atoms occupy random interstitial positions in the UO_2 lattice, by an ordering process involving an appreciable entropy and enthalpy change.[16] The conclusion seems to be that the susceptibility maximum at 6·4°K is not a function of the complex, ordered structure of U_4O_9.

Another type of ordering is presumably involved in the β-U_3O_7 structure, giving rise to the marked tetragonal distortion of the fluorite cell. The susceptibility results indicated very similar behaviour to that of U_4O_9, with a maximum at much the same temperature and larger absolute values of χ. Again, no corresponding anomaly was observed in measurements of the specific heat.[14]

Rather surprisingly then, it seems that the magnetic behaviour of these materials (as measured by a low-field a.c. method) is not closely related to the thermal properties, and is independent of the details of the structure, depending mainly on the excess of oxygen in these phases based on the structure of UO_2. The nature of this dependence is at present not understood; it may be a function of the valency state of the uranium ions.

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[16] Roberts and Walter, *J. Inorg. Nuclear Chem.*, 1961, **22**, 213; Markin and Roberts, "Thermodynamics of Nuclear Materials," I.A.E.A., Vienna, 1962, 693.